Cubic Phase GaN Integrated on CMOS-Compatible Silicon (100)

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Abstract

We report a method of synthesizing pure cubic phase GaN integrated on Si(100) platform using the novel aspect ratio nano-patterning. We demonstrated through modelling and experiment data that complete cubic phase GaN epilayer coverage can be achieved when critical silicon patterning parameters are met. The purity and quality of the resulting cubic phase GaN are verified using temperature dependent cathodoluminescence, atomic force microscopy and electron backscatter diffraction. Acceptor energies, Varshni coefficient, surface roughness, spectral and spatial quality are reported.

INTRODUCTION

GaN semiconductors offer unique opportunities for ultraviolet-visible-infrared photonics due to its wide range of tunable bandgap (0.88 ~ 6 eV), and for power transistors due to its high breakdown voltage and saturation velocity. Almost without exception, GaN photonics and other devices are fabricated on the thermodynamically stable hexagonal (wurtzite) material phase. Due to the lack of inversion symmetry in wurtzite/hexagonal (h-) phase GaN lattice, devices based on the c-plane of this material phase possess inherent spontaneous and piezoelectric polarization fields that point in the direction of material growth <0001>. These fields are detrimental to photonics (through reduced radiative recombination rates caused by quantum confined stark effect), and to power electronics (through dictating normally-on operation). Other h-phase GaN crystal facets, such as the semi-polar r-plane and the non-polar m-plane, of the h-GaN material have also been explored for polarization-free semiconductor devices. However, these substrates suffer from low availability and poor material quality.

Due to its centrosymmetric properties, zinc-blende/cubic (c-) phase GaN is inherently polarization-free. Additionally, it has properties (higher hole mobility doping efficiency) beneficial for radiative recombination, and its smaller bandgap (E_G = 3.22 eV) necessitates a smaller indium mole fraction to emit at wavelengths in the green/yellow range in comparison to h-GaN (E_G = 3.42 eV). However, its phase metastability on conventional planar substrates (GaAs, 3C-SiC) has prohibited its synthesis. GaN grown via this approach often results in highly defective and mixed phase material.

Recently, a novel method of cubic phase GaN synthesis – hexagonal-to-cubic phase transition – was introduced through the novel aspect ratio nano-patterning of on-axis, CMOS compatible Si(100) substrates via MOCVD [1]. Using KOH anisotropic wet etching of Si on substrate patterned with SiO_2, U-shaped grooves with a SiO_2 – Si(111) – Si(100) – Si(111) – SiO_2 surfaces are created (Fig. 1a-c). The h-phase GaN crystals, selectively nucleated on the {111} surfaces, will meet at an angle of 2×54.7° = 109.5°, which is also the angle between two tetrahedron bonds. The GaN thereafter will phase transition to form c-phase GaN after the crystals merge. The choice of on-axis, 750 µm thick-200 mm diameter Si(100) as the substrate makes this approach inexpensive, compatible with existing large scale fabrication techniques, and integrable with Si logic devices and silicon photonics. Here we report on the scalability, phase purity, and reproducibility of this technology that could enable Si-integrated nano c-phase GaN devices for next generation photonics and electronics.

MODELLING

A schematic of the crystallographic growth dynamics of the GaN in a nano-patterned U-groove seen from the cross section is shown in Fig 1a. The dielectric/GaN and Si/GaN boundaries are indicated by the dash-dot red and solid turquoise lines, respectively. The c-GaN will grow in a triangular shape as indicated by the blue dashed line. For complete c-phase GaN surface coverage in these U-grooves, the top side of the blue dashed triangle has to cover the entire dielectric opening. This is achieved when the deposition thickness, *h,* defined as the GaN deposition thickness above Si(100) substrate surface, equals to the critical thickness (h_c):

$$h_c = (1.06p - 0.75t_d) \Big/ \left(1 - \frac{\tan\alpha}{0.71}\right)$$

where p is the opening width of the U-groove at the dielectric/substrate interface, t_d is the silicon etch depth, and α is the dielectric sidewall angle (Fig. 1a) [2]. Additionally, the dielectric sidewalls need to be high enough to contain the GaN grooves to prevent an overgrowth. Here we define a ratio, $ff = \frac{h}{h_c}$, to quantify how optimized a given U-groove is

for pure c-GaN surface coverage. A *ff* < *1* indicates that the c-phase GaN triangle is too small, and more GaN growth is required. Conversely, if *ff* > 1, too much GaN has been deposited. This results in formation of very defective and mixed phase material growth.

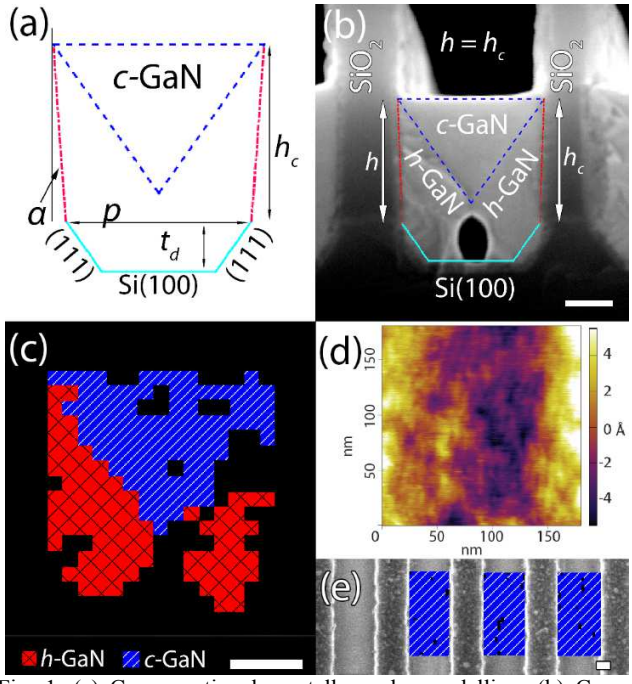

Fig. 1. (a) Cross sectional crystallography modelling; (b) Cross-sectional SEM image; (c) EBSD image of the GaN growth in a nano-patterned U-groove; (d) AFM image of the c-phase GaN surface (RMS roughness of 2.65 Å); (e) Multi-period plane-view SEM/EBSD overlay. Scale bar = 100 nm.

RESULTS

At the critical thickness, $h = h_c$, c-phase GaN covers the entire epitaxial surface; this can be seen from the cross-sectional SEM image (Fig. 1b). Electron backscatter diffraction (EBSD) phase detection, showing the GaN phases in red-crossed (hexagonal) and blue-striped (cubic) pixels, corroborates our modelling (Fig. 1c), showing very clear phase separation after the h-phase crystals coalesced at the bottom of the dashed-blue triangle. Atomic force microscopy (AFM) conducted on the c-phase GaN epilayer in tapping mode reveals a very smooth, device ready epilayer with a root mean square (RMS) roughness of 2.65 Å. No threading dislocation, a characteristic defect commonly seen in h-GaN with density $>10^8$ cm^{-2}, can be observed.

The reproducibility of the c-phase GaN integrated on Si (100) can be observed via a large scale 3-groove plane-view EBSD overlaid on SEM image of a field of U-grooves (Fig. 1e). No detectable h-phase GaN crystals (red-crossed pixels) were observed from the top. The nano-groove field can in principle cover the entire substrate, providing an unprecedentedly large 200 mm diameter substrate for c-phase GaN.

The high quality c-phase GaN synthesized through the phase-transition method opens up a path to study the fundamental properties of the cubic phase of GaN. A temperature dependent Cathodoluminescence (CL) is conducted to study and compare the band structures of the two phases of GaN on Si(100) [3]. By adjusting the electron acceleration voltage, CL can create electron-hole-pairs in the very top layer only (2 kV yields a 50 nm penetration depth). Additionally, CL can verify the phase purity through the presence and intensity of c- and h-phase GaN bandgap emissions.

Fig. 2 shows the room temperature (294 K) CL spectra of eleven different configurations of U-grooves. The SEM is set to rostering mode with electron acceleration of 2 kV and a measured current of 2 nA. This allows the examination of the top layer (~ 47 nm) over an area of roughly 50 × 30 μm^2. The vertical blue-dotted line and the red-dashed line represent the near band edge emission of c-phase and h-phase of GaN respectively, as a guide to the eye for distinguishing emission centers. The U-grooves with *ff* = 0.95 show a very clean c-phase GaN bandgap emission with no detectable h-phase GaN signals. For the U-grooves with *ff* < 1, an increasing (decreasing) c-phase (h-phase) emission intensity is observed as *ff* increases. This suggests the increasing (decreasing) c-phase (h-phase) GaN surface coverage as more GaN is deposited. In the case of over-deposition of GaN in the grooves, represented by *ff* > 1, the spectra show a superposition of band edge emission from both phases and/or a widened FWHM. This indicates the phases are mixing at the surface in these configurations, and the crystalline qualities suffer as the result.

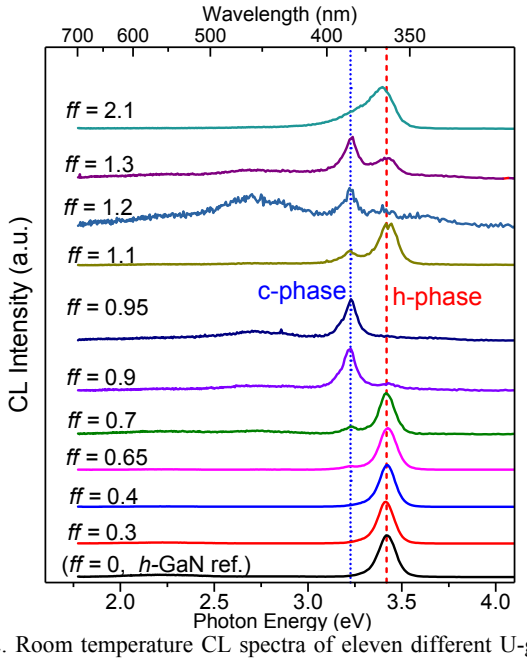

Fig 2. Room temperature CL spectra of eleven different U-groove fill factors (*ff*). The blue-dotted and red-dashed lines represent the near band edge emissions of c-phase and h-phase GaN.

To study the phase purity, crystalline quality, and defect levels associated with the phase transitioned c-phase GaN, a temperature dependent cathodoluminescence study was conducted from 5.7 K to room temperature. Fig. 3 shows a comparison between the spectra of 5.7 K (solid line) and 280 K (dotted line) of h-phase GaN (Fig. 3a) and c-phase GaN (Fig. 3b).

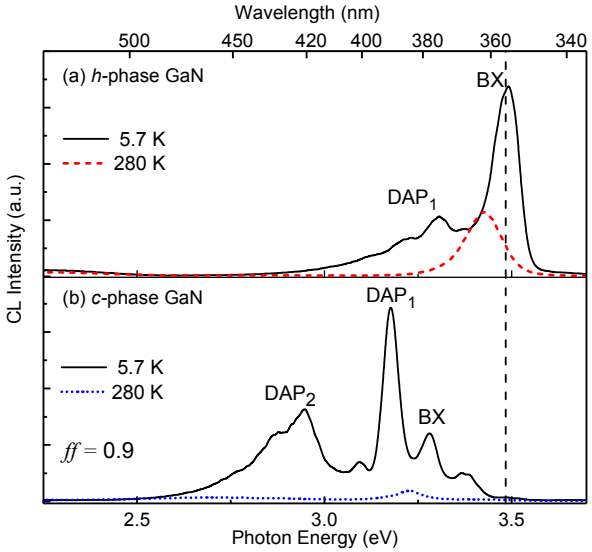

Fig 3. CL spectra of (a) h-phase GaN, and (b) c-phase GaN at 280K (color-dotted lines) and at 5.7K (black-solid lines).

At 5.7 K, bound excitons (BX), and donor-acceptor pairs (DAP_x) and their LO-phonon replica transitions can be seen. The vertical dashed line represents the BX transition of h-phase GaN. It is evident that no h-phase GaN emission (vertical dashed guide line for the eye) is present in the c-phase GaN CL spectrum.

In order to verify the origin and nature of these radiative recombination centers, an injection current dependent CL study was conducted at 5.7 K. Fig. 4 shows the CL spectra of the *ff* = 95% U-grooves with electron beam current between 0.2 ~ 3.2 nA. The following expression is used to calculate the electron-hole-pair generation rate [5]:

$$G = \frac{I_b V_b (1-\gamma)}{q \times V (2.8E_g + 1)}$$

where I_b is the electron beam current, V_b the electron beam voltage (2 kV), γ the electron backscatter coefficient (~0.05), q the fundamental charge, V the electron beam interaction volume, and E_g the bandgap energy (~3.3 eV) of c-phase GaN. The interaction volume is estimated as a sphere with diameter determined by the Kanaya-Okayama formula [6]:

$$D = \frac{0.0267 \times A \times E_0^{5/3}}{\rho \times Z^{8/9}}$$

where D is the maximum electron penetration depth, A the atomic weight, E_0 the beam energy, ρ the density, and Z the weighted average atomic number. The equation yields a depth of 44 nm at 2 kV of electron acceleration voltage. The estimated G is between 0.54 to $8.7 \times 10^{27} cm^{-3} s^{-1}$ for injection current of 0.2 ~ 3.2 nA.

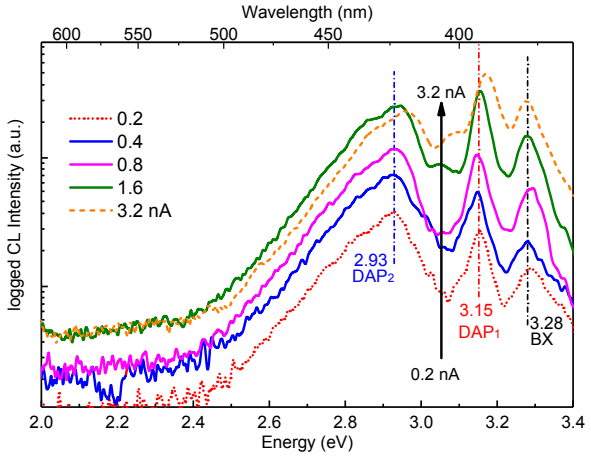

Fig 4. CL spectra of the *ff* = 0.95 U-grooves at 5.7 K with injection current ranging from 0.2 to 3.2 nA.

At 3.2 nA (orange-dashed line), both DAP_1 and DAP_2 show a very strong blue shift in emission energy – a characteristic of DAP emissions. Under intense carrier injection/generation, electrons bound to donors recombine with more distant, and therefore less columbic attraction, holes bound to acceptors. This results in a higher energy transition. A very distinct saturation in intensity is also observed. These observations support the designation of the radiative recombination centers as DAPs. In contrast with the DAPs, the BX line shows no shift in energy and saturation, this is a characteristic of a band to band transition, where the density of states is practically infinite.

The evolution of energies of different c-phase GaN emission centers is studied via varying the temperature. The bandgap shrinkage (Fig. 5, black short-dashed and solid lines, and squares), as a function of temperature, can be modelled using Varshni's equation [4]:

$$E_g(T) = E_0 - \frac{\alpha_v T^2}{(T + \beta)}$$

where E_0 is the bandgap at zero temperature, α_v is the Varshni's coefficient, and β is taken as the Debye temperature of GaN (600 K). Least square fit yields $E_0 = 3.31\ (\pm\ 0.01)\ eV$ and $\alpha_v = (6.83 \pm 0.22) \times 10^{-4}\ eVK^{-1}$ for c-phase GaN.

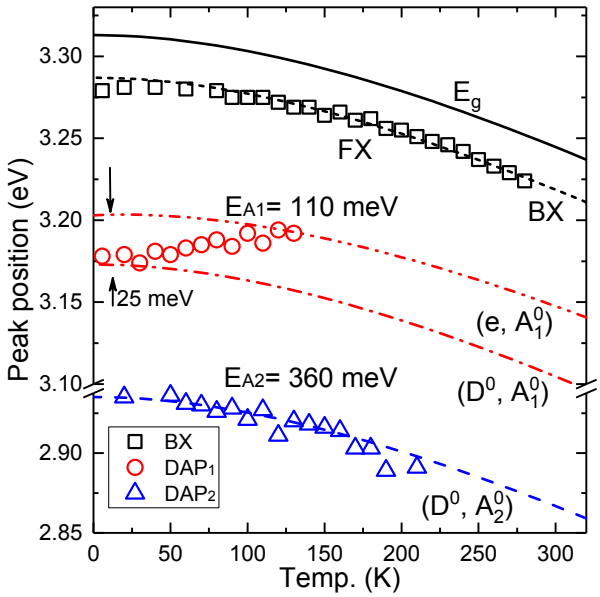

Fig 5. Temperature dependence of emission centers of phase transitioned c-phase GaN from 5.7 K to 280 K.

The DAP_x transitions (D^0, A_x^0) follows:

$$h\nu\left(D^0, A^0\right) = E_g - E_D - E_A + \eta N^{\frac{1}{3}}$$

where

$$\eta = \left(\frac{4\pi}{3}\right)^{\frac{1}{3}} \times \frac{e^2}{4\pi\varepsilon\varepsilon_0}$$

where, E_D is the donor level (~20 meV, silicon), E_A the acceptor level, N is the dopant concentration ($10^{16}\,cm^{-3}$ for unintentionally doped GaN), η is a material property (for GaN, $\varepsilon = 9.7$, $\eta = 2.39 \times 10^{-8} eV\,cm$). For c-phase GaN, the calculated acceptor energies are E_{A1} = 110 meV and E_{A2} = 360 meV for DAP_1 (red dotted-dashed lines and circles) and DAP_2 (blue long-dashed line and triangles), respectively. As temperature increases from 5.7 K, DAP_1 transitions from a donor-to-acceptor (D^0, A_1^0) recombination to a free-to-acceptor pair (e, A_1^0). We attribute DAP_2 (D^0, A_2^0) to intrinsic defects such as gallium vacancy (V_{Ga}), a common defect in MOCVD grown GaN [7].

A small shift away for the fitted line at temperature < 50 K in the near band edge transition at ~ 3.28 eV is attributed to the change from free exciton (FX) to bound exciton recombination as temperature decreases. The total shift is on the order of ~6 meV. The lack of a (D^0, A_1^0) to (e, A_1^0) type blue shift in energy (~ 25 meV) as temperature increases indicates that the 3.28 eV emission seen in c-phase GaN is comprised of solely band-to-band type transition, and not a superposition with h-phase GaN's DAP_1. This in turn demonstrates the phase purity of c-phase GaN on the surface of the U-grooves in the most optimized configuration of the U-grooves.

Conclusions

We report phase transitioned c-phase GaN grown on Si(100) via nano-patterning shows excellent purity, reproducibility, and scalability via crystal growth modelling and experiments. Room temperature CL conducted in rostering mode revealed the importance of U-groove configuration and GaN deposition thickness for pure c-phase GaN surface coverage. Temperature dependent CL studies identified two acceptor energies (110 and 360 meV) and the Varshni coefficient ($\alpha_v = 6.83(\pm 0.22) \times 10^{-4} eVK^{-1}$) of the temperature dependence of the bandgap energy in c-phase GaN. Additionally, AFM shows a device ready root-mean-squared surface roughness of 2.65Å. EBSD and CL study show a phase purity and crystal quality with very controlled growth and large surface reproducibility that have not been observed in conventional planar grown c-phase GaN on other more expensive substrates. Phase-transitioned c-phase GaN has shown its potential to become the substrate of choice for next generation polarization-free photonics and electronics integrated on Si(100).

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Acronyms

MOCVD: Metalorganic chemical vapor deposition
SEM: Scanning Electron Microscopy
EBSD: Electron Backscatter diffraction
CL: Cathodoluminescence
FWHM: Full Width at Half Maximum